

ADSORPTION OF TRACE STEROID ESTROGENS TO HYDROPHOBIC HOLLOW FIBRE MEMBRANES FROM AQUEOUS PHASE

Sheng Chang, * T. David Waite, *Andrea I. Schäfer, **Anthony G. Fane,

*Centre for Water and Waste Technology, School of Civil and Environmental Engineering,
UNSW, Sydney, NSW 2052, Australia, D.Waite@unsw.edu.au

**UNESCO Center for Membrane Science and Technology, School of Chemical Engineering and
Industrial Chemistry, UNSW, Sydney, NSW 2052, Australia,

ABSTRACT

This paper discusses adsorption of estrone to microfiltration hollow fibre membrane from aqueous phase using estrone as the model compounds. The partitioning of estrone between membrane and aqueous phase at equilibrium state, the concept of membrane retention towards estrone caused by adsorption, adsorption kinetics, and the application potential of membrane adsorption have been assessed through batch adsorption and dead-end filtration of solution containing trace estrone. The results show that adsorption could result in significant accumulation of estrone on membrane surface. The partition of estrone between membranes and aqueous phase can be characterized by the Freundlich equation. The microfiltration membrane could exhibit high retention to estrone due to adsorption but the retention decrease with the increase in estrone amount accumulated on the membrane surface. Implication of this study is of an important nature, especially in drinking water applications. Contaminants such as natural and synthetic hormones may accumulate on the membranes and desorb during backwash or membrane cleaning. Further studies are needed to address risk issues involved

INTRODUCTION

Although field data suggested that modern activated sludge treatment processes could consistently remove most of synthetic and natural hormones that enter the works (Johanson and Sumpter, in press), the steroid estrogens still appear to be the most potential endocrine disrupters in sewage effluent [Johnson and Sumpter, in press]. These trace compounds, usually in the range of 1 to 30 ng/L, could exert significant effect on biota exposed in the receiving environment such as feminisation of male fish [Sumpter and Jobling, 1995]

Since estrogens are hydrophobic organic compounds of low volatility, sorption could play an important role in removal of these compounds. Johanson and Sumpter (in press) reviewed removal of endocrine-disrupting chemicals in activated sludge treatment works. They suggested that the principle mechanisms for steroid estrogens removal in the activated sludge processes could be sorption and biodegradation. In generally, for more hydrophobic compounds like synthetic steroid 17 α -ethinylestradiol (EE2, logK_{ow} ~ 4.1, Lai et al. 2000), sorption to sludge is likely to play a more important role in removal of those compounds, while for relatively weakly hydrophobic compounds like Estriol (E3) binding to the sludge could be a less dominated factors. Lai et al [2000] studied binding of steroid estrogens to river sediment using well controlled adsorption experiments with the solution spiked to a concentration of 0.1 mg/mL. The results showed that sorption could be a significant factor in reducing aqueous phase concentrations of steroids estrogens. In addition, some results about adsorption of nature hormones to MIEX and activated sludge have also been reported in a local workshop proceedings by Schäfer et al (2002).

Microfiltration hollow fibre membranes have widely been used in water reuse and treatment. Our studies showed that significant natural hormones could be accumulated on hydrophobic hollow fibre membranes due to sorption. This phenomenon could exert important impact on hormone

removal and fate in water treatment system where membranes are used for a process barrier. In the present paper, the characteristics of partition of estrone between solution and membranes, the concept of membrane retention due to adsorption, adsorption kinetics, and application potential of membrane adsorption for estrone are discussed.

EXPERIMENTAL

Flask adsorption and dead-end filtration tests were carried out to assess the adsorption characteristics of estrone on hollow fibre membranes. The flask experiments were carried out in an incubator (Bioline, Edwards Instrument Company Australia) under conditions of 250 rpm and 25 °C and 50 mL solution. For dead-end filtration, a small bundle of hollow fibre membranes, which had a filtration area about 0.00058 m², was directly immersed in the test solutions and a peristaltic pump (Masterflex 7518-00, Cole-Parmer Instrument Company) was used to pump the permeate out from the fibre lumen. The membrane used was a hydrophobic 0.2 μ m USFILTER hollow fibre membrane. The mean outer and inner diameters of the hollow fibre were 0.65 mm and 0.39 mm for the USFilter fibre. All the hydrophobic membranes tested were wetted by 50% alcohol solution before experiments.

1m M NaHCO₃ and 20 mM NaCl, which provided buffering to about pH 8 was used as the background solution. Estrone was used as the model solutes. The test solutions were prepared by dissolving a certain amount of ³H-labelled estrone in the background solutions. The radiolabeled estrone was purchased from Sigma Aldrich (Saint Louis, Missouri, USA). A Packard Instruments scintillation counter which has a detection limit of approximately 0.1 ng/L for estrone was used for analysis of the radiolabeled compounds.

RESULTS AND DISCUSSIONS

Partitioning of estrone to hydrophobic membrane.

The characteristics of estrone partitioning between membrane and solution was assessed by static adsorption experiments which were carried out by placing a selected amount of hollow fibre membranes into a number of flasks which contained estrone solution of a specific initial concentration. The mixture of the membranes and the estrone solution was then shaken for 24 hours at constant temperature until an equilibrium concentration (C_e) was reached. Figure 1 shows the relationship between the concentration drop (100*(C₀-C_e)/C₀) and organic loading which was defined as the ratio of estrone concentration to membrane mass per unit volume solution. These results showed that the estrone removal decreased with the increase in organic loading due to the decreased adsorbent for a given initial concentration.

The amount of solute adsorbed per unit membrane mass at the equilibrium state can be calculated from mass balance:

$$C_{se} = \frac{V_0(C_0 - C_e)}{m_s} \quad (1)$$

Where V₀ is the volume of the solution, C₀ is the initial concentration, m_s is membrane weight. Before the adsorption sites are completely saturated by sorbate the amount of sorbate accumulated on the adsorbent surface depends on the supply of sorbate in the solution. When the sorbate in the solution approaches exhaustion. Such an adsorption equilibrium can be characterized by the relationship between the solution concentration and the surface concentration at the equilibrium state or (isotherm relationship). The lower the solution concentration the lower the surface concentration. Based on batch adsorption data, estrone partitioning between the membrane tested and the solution at equilibrium could be described by Freundlich equation in concentration range of 1.3 to 42 ng/L:

$$C_{se} = 3.39C_e^{1.30} \quad (3)$$

The constant in equation 3 has been determined using least square methods according to the experimental results. Figure 2 shows that the experimental equilibrium relationship can be well described by the empirical isotherm equation.

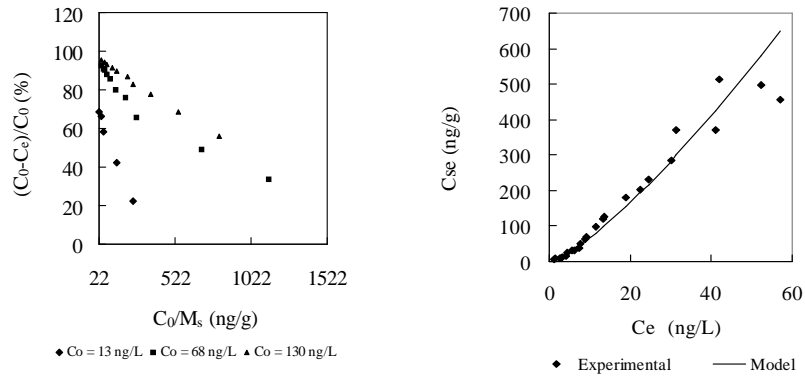


Figure 1 Effect of organic loading on decrease in solution concentration

Figure 2 Experimental and predicted isotherm relationships for estrone adsorption to the hollow fibre membranes tested

Retention caused by adsorption

The filtration of solutions containing trace estrone showed that microfiltration membranes could exhibit a temporary high retention to estrone due to adsorption. Assuming that an equilibrium partitioning of estrone to the membrane could be built up on passage of the solution through the membrane, the concentration of the permeate is a function of the amount of estrone accumulated on the membrane surface (C_{st}) (adsorption and desorption equilibrium) and could be described by the isotherm relationship:

$$C_p = 0.39C_{st}^{1.30} \quad (4)$$

and the membrane retention (R) caused by adsorption could be expressed as:

$$R = 1 - \frac{C_p}{C_i} = 1 - \frac{0.39C_{st}^{1.30}}{C_i} \quad (5)$$

From equation 5 it can be noted that the membrane retention of estrone will decrease with the increase in the amount of estrone accumulated on the membrane surface. When the surface concentration reached the equilibrium value corresponding to the estrone concentration in the influent membrane retention will become zero or no further adsorption of estrone from the influent to the membrane surface will occur. Figure 3 showed the change in membrane retention in dead-end filtration of estrone solution of different concentrations. It can be seen that the estrone retention by the membrane decreases with time and the retention finally becomes negligible as the adsorption capacity is exhausted.

The time taken to get the membrane saturated depends on the rate of adsorption. Batch adsorption experiments were carried out to assess the kinetic behavior of estrone adsorption to the membrane

surface. Figure 4 shows results obtained in batch adsorption experiments in which a certain amount of membrane were placed into flasks which contained estrone concentration of different initial concentration. The experiments indicated that the adsorption rate was very high in the first one hour, then following an about two hour slow sorption prior to an adsorption equilibrium state.

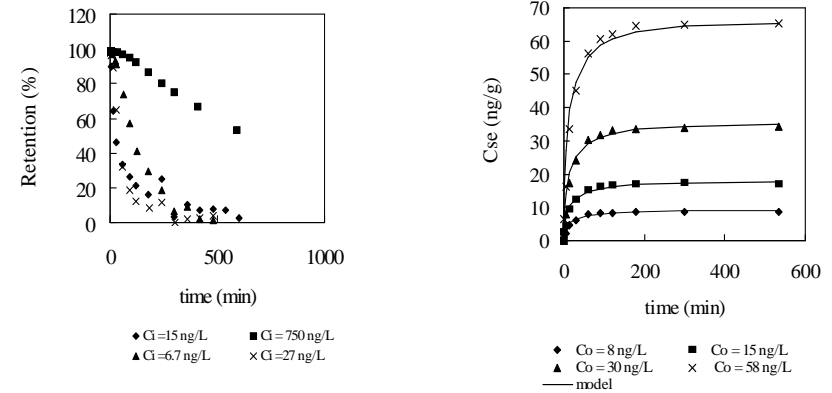


Figure 3 Decrease in membrane retention with time during dead-end filtration of estrone solution

Figure 4 Experimental and simulated kinetic behavior of estrone adsorption to the membranes (batch adsorption).

The transportation of estrone to the hollow fibre membrane may be comprised of bulk solution transport, boundary layer film transport, internal pore transport, and adsorption. The bulk transport is the transport from the bulk solution to the boundary layer next to the membrane surface and can be caused by diffusion or turbulent mixing. The flask adsorption experiments in this study were carried out in an incubator with shaker speed of 250 rpm so the mixing was vigorous enough to assume the bulk solution has a homogenous concentration distribution. The boundary layer film transport is the molecular diffusion through the stationary boundary layer to the membrane surface and the pore entrance. After the estrone enter the pore, estrone must be transported through diffusion to an available site, where an adsorption bond between estrone and membrane can be formed. The adsorption could be considered diffusion controlled if diffusion is much slower than adsorption, and reaction controlled if the opposite is true. Jones and O'Melia studied BSA and Humic acid adsorption onto hydrophilic membrane surfaces and suggested following equations for diffusion and reaction limited adsorption, respectively.

$$C_{st} = C_{se} \left\{ 1 - \exp \left[\left(\frac{-2C_0\alpha}{C_{se}} \right) \left(\frac{Dt}{\pi} \right)^{1/2} \right] \right\} \quad (6)$$

$$C_{st} = C_{se} (1 - e^{-k_0 t}) \quad (7)$$

where D is diffusion coefficient, α is rate ratio of 0 to 1, describing the degree to which adsorption is controlled by diffusion, and k_0 is a kinetic constant. The diffusion controlled model (Eq 6) has been developed from one-dimensional diffusion equation with introducing a term to consider the effect of site availability, while the reaction controlled adsorption model (Eq 7) has been built up based on Langmuir kinetic equation. Fitting our batch adsorption data to the above models shows that the kinetic behaviour of estrone adsorption to the membrane could be well described by the

diffusion controlled model but not by the reaction controlled model. Figure 4 shows the kinetic behaviour predicted the diffusion controlled model with setting $\alpha = 0.065$ and $D = 1.835 \times 10^{-6} \text{ cm}^2/\text{s}$ (calculated from Stokes-Einstein equation). However the small value of α for the adsorption implies that diffusion is not the rate controlling mechanism for the adsorption. Given the fact that a term considering the site availability has been introduced into the diffusion controlled model, it may be reasonable to presume that site availability could be a limiting step for adsorption of estrone to the hollow fibre membranes.

The time membrane taken to get the membrane saturated could be calculated by combining the isotherm relationship with equation 6. The calculation showed that the membrane could be saturated very quickly if estrone could be delivered to the membrane surface quick enough (no transport limitation as batch adsorption). However for a practical system, the rate of accumulation of estrone on the membrane surface could be limited by estrone transportation through the bulk solution or input to the system so the time taken to get the membrane saturated will be strongly system dependent.

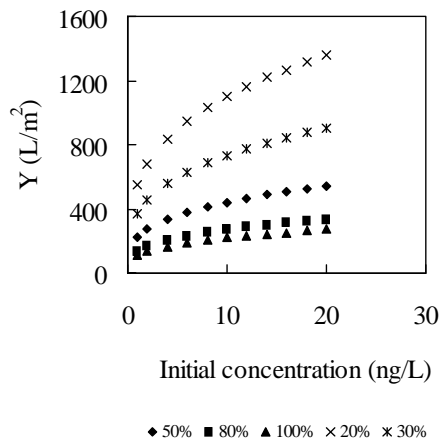


Figure 5 Effect of different removal degree and influent concentration on Y

Application potential of membrane adsorption.

Isotherms can be used to obtain a rough estimate of the capacity of adsorption of the membrane to estrone. Assuming that all of the membrane in a system will reach equilibrium with the adsorbent influent concentration (C_i), the volume of water can be treated by per unit membrane area for a specified removal (ϕ) can be calculated by:

$$Y = \frac{C_{se}}{C_i \phi} \gamma = \frac{3.39 C_i^{0.30}}{\phi} \gamma \quad (8)$$

where γ is the mass of membrane per m^2 . Figure 5 shows the effect of different removal degree and influent concentration on Y. From this figure it can be seen that Y increases with increase in influent concentration and decrease in removal degree. Given the limited capacity of the membrane, it does not seem to be a practical idea to use membrane adsorption for trace hormones removal for large-scale water treatment. However, considering the fact that the tested membrane could adsorb trace estrone from aqueous phase very effectively and could be easily eluted from the membranes, it appears to be possible to make use of such characteristics of the membrane for sample treatment in

trace hormones analysis. A further study on competitive adsorption and elution could be of interests for such an application.

CONCLUSIONS

In this paper adsorption of estrone to hydrophobic microfiltration hollow fibre membrane from aqueous phase has been discussed. The partitioning of estrone between membrane and aqueous phase at equilibrium state, the concept of membrane estrone retention caused by adsorption, adsorption kinetics, and the application potential of membrane adsorption for estrone have been discussed. The results show that adsorption could result in significant accumulation of estrone on the membrane surface. The partitioning of estrone between membranes and aqueous phase can be characterized by Freundlich equation. The microfiltration membrane could exhibit high retention to estrone due to adsorption but the retention decrease with the increase in estrone amount accumulated on the membrane surface leading to breakthrough. Implication of this study is of an important nature, especially in drinking water applications. Contaminants such as natural and synthetic hormones may accumulate on the membranes and desorb during backwash or membrane cleaning. Further studies are needed to address risk issues involved.

ACKNOWLEDGMENT

Funding for this research was provided by Queensland Government and the Australian Research Council (SPIRT Scheme).

REFERENCES

- Johnsin, A. C., Sumpter, J. P., Removal of endocrine-disrupting chemicals in activated sludge treatment works, Environmental Science and Technology (in press).
- Jones, K. L. O'Melia, C. R., 2000, Protein and humic acid adsorption onto hydrophilic membrane surface: Effects of pH and ionic strength, J. Membrane Sci., 165, 31-46.
- Lai, K. M., Johnson, K. L., Scrimshaw, M. D., Lester, J. N., 2000, Binding of waterborne steroid estrogens to solid phases in river and estuarine system.
- Shäfer A. I., Waite, T. D., Sherman (Eds.), 2001, Recent advanced in water recycling technology, Workshop proceedings, Brisbane, QLD, Australia.
- Sumpter, J. P., Jobling, S., 1995, Vitellogenesis as a biomarker for estrogenic contamination of the aquatic environment. Environ. Health Perspect 103, 173-178.

CONTACT

Professor T. D. Waite
Centre for Water and Waste Technology,
School of Civil and Environmental Engineering,
UNSW, Sydney, NSW 2052, Australia,
D.Waite@unsw.edu.au, Tel: 61-2-93855060, Fax: 61-2-93856139